

The Role of Soil Organic Matter Structure in Controlling the Desorption and Bioavailability of Organic Compounds

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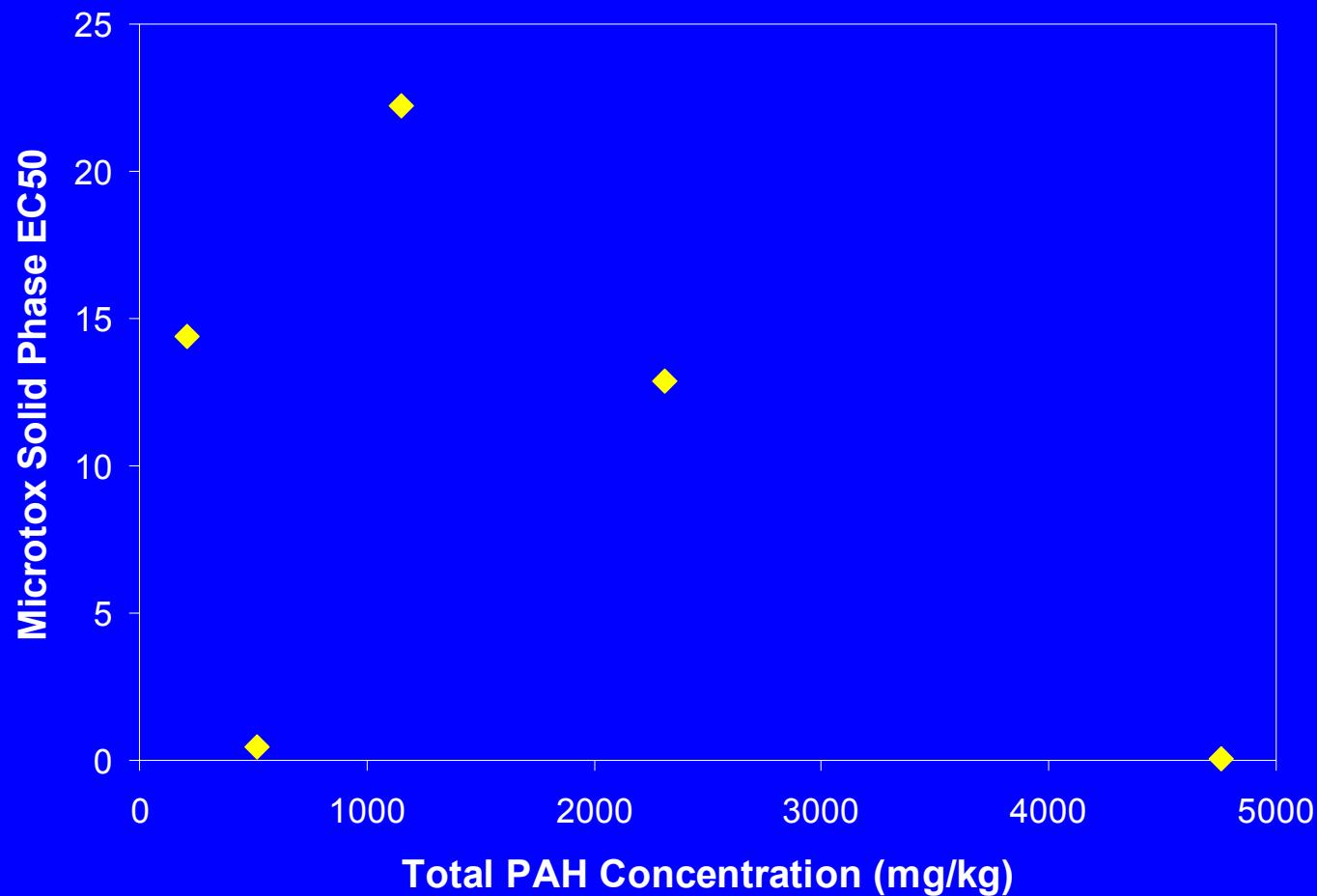
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What We Know

- Total extractable organic contaminant concentrations are a poor surrogate for predicting the risk posed by contaminated soils and sediments.
- A portion of the organic contaminants extractable under vigorous conditions appears to be “unavailable” to cause deleterious effects (or to be easily remediated).

Example: Lack of relation between total concentrations and toxicity for 5 MGP soils



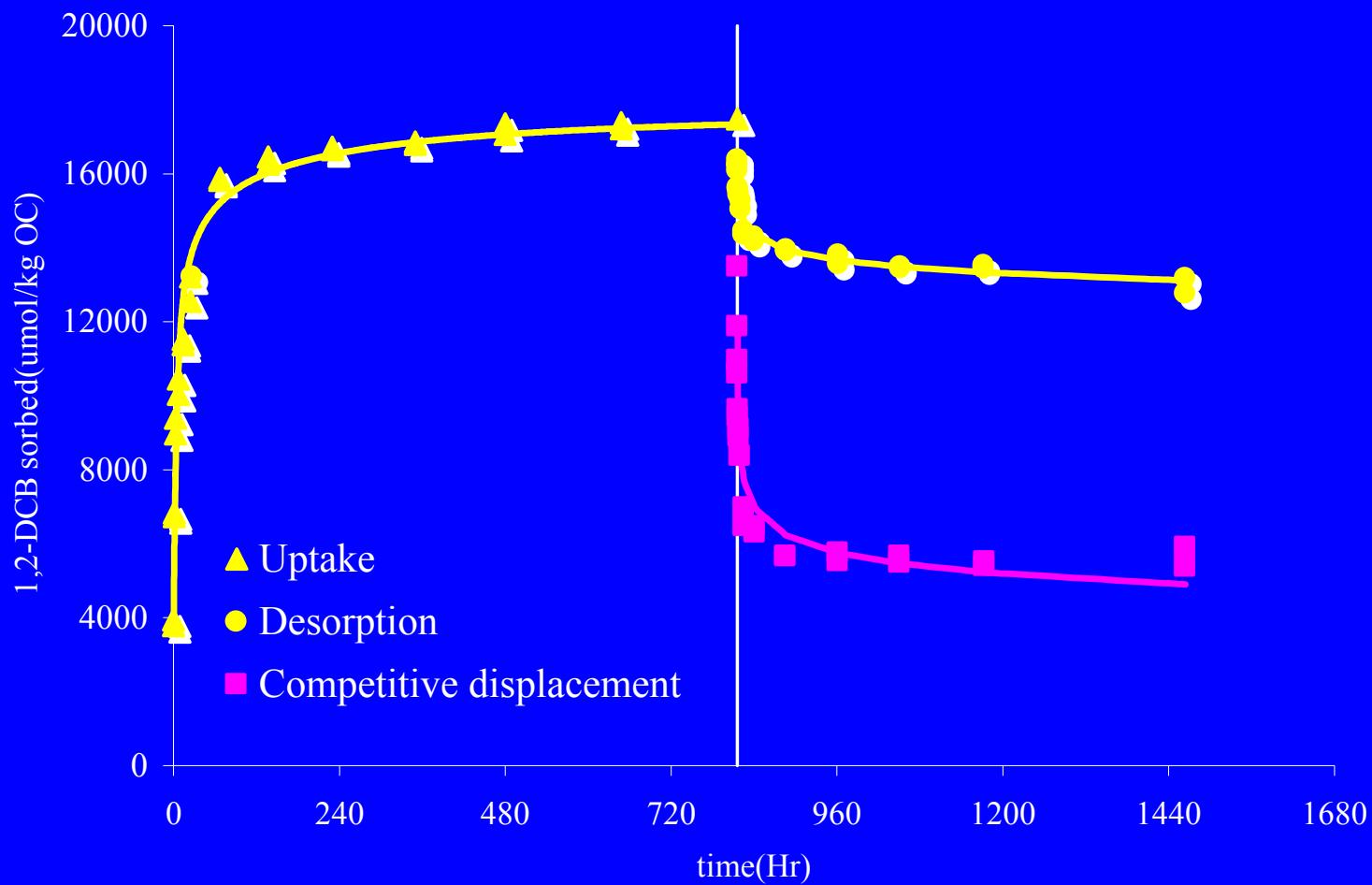
What We Don't (Precisely) Know

- Why a fraction of the bound contaminant is not bioavailable.
- Key variables determining bioavailability
 - *Nature of contamination*: contaminant characteristics, aging time, concentration
 - *Biological factors*: species characteristics, especially strategies for promoting release such as surfactants, pH alteration and the kinetics of uptake/transformation
 - *Environmental factors*: temperature, moisture, solution composition
 - *Soil/sediment factors*: organic matter and mineral composition, particle/aggregate size

Why We Should Care about What We Don't Know

- Regulators and the public are not comfortable leaving contaminant in place when the reasons for (and permanence of) its unavailability cannot be clearly articulated.
- As a result of our lack of knowledge, society spends significant (likely unnecessary) resources to remediate contaminants posing little, if any, threat to human health or the environment.

Example: Concern About Competitive Remobilization of Sorbed Species



Working Hypotheses

- Desorption resistant organic chemicals are mainly associated with condensed (possibly rigid/glassy) SOM domains.
- Slow desorption of chemicals from these domains limits the ultimate rate and extent of biodegradation
- Advanced SOM characterization methods can be used to identify the structural features leading to desorption resistance

Study Design—Sorption/Bioavailability

- Phenanthrene used as hydrophobic probe
- Bottle point adsorption isotherms (7d)
- Bottle point desorption isotherms after freeze drying (7d)
- Batch desorption rate studies using Tenax as infinite sink
- Mineralization rates measured with phenanthrene degrading bacterial inoculum

Materials

	OC (wt%)	N (wt%)	C/N	Free (mg/g OC)		Amorphous (mg/g OC)	
				Fe	Al	Fe	Al
Tinker	11.0	0.49	22.4	195.8	139.5	37.8	93.4
Forbes	4.30	0.19	22.6	4463.3	462.1	109.5	286.7
Yolo surface	1.20	0.14	8.6	3,738.3	409.2	151.7	60.0
Yolo vadose	0.32	0.04	8.0	11,675.0	1,406.3	868.8	250.0
Houghton	46.1	3.10	14.9	55.2	14.3	28.0	2.8
Chelsea	5.60	0.29	19.3	1,572.5	100.7	161.6	22.7
Webster	2.97	0.14	21.2	598.3	300.0	58.2	39.7
Ohio shale	2.44	ND	--	677.5	141.8	141.0	21.3

Examples of Soil Variability

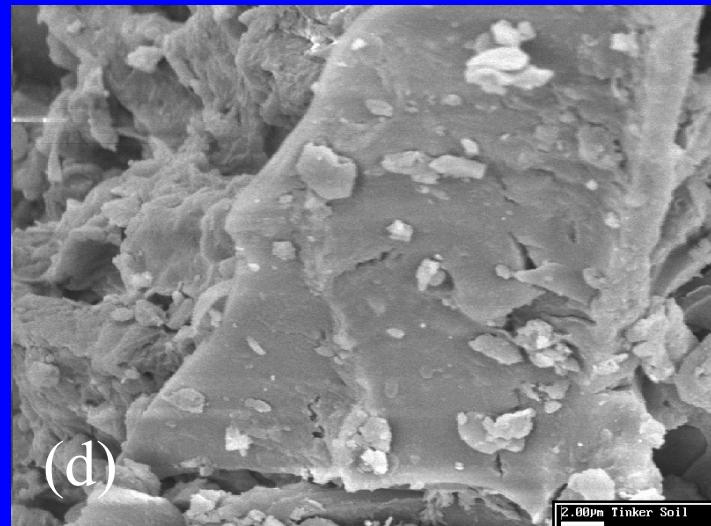
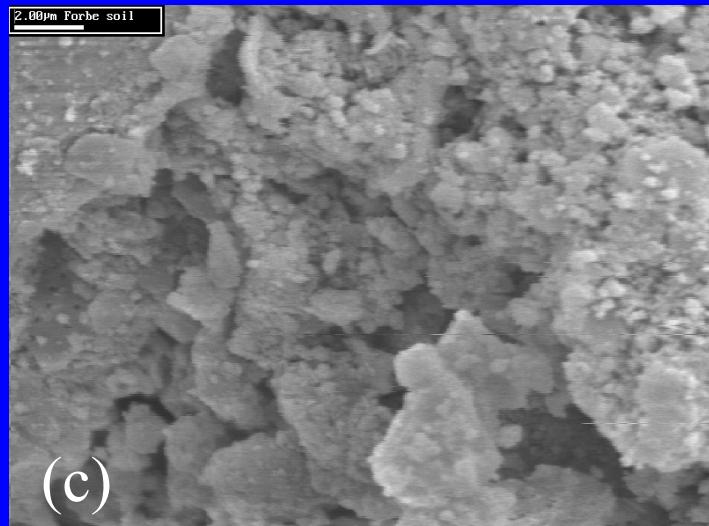
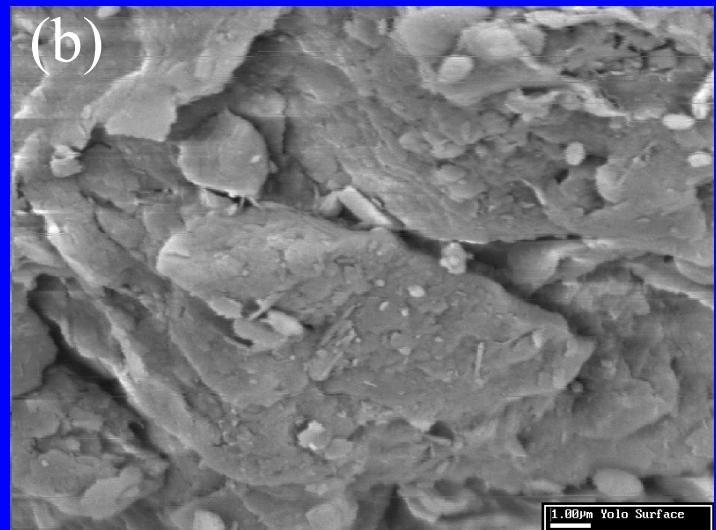
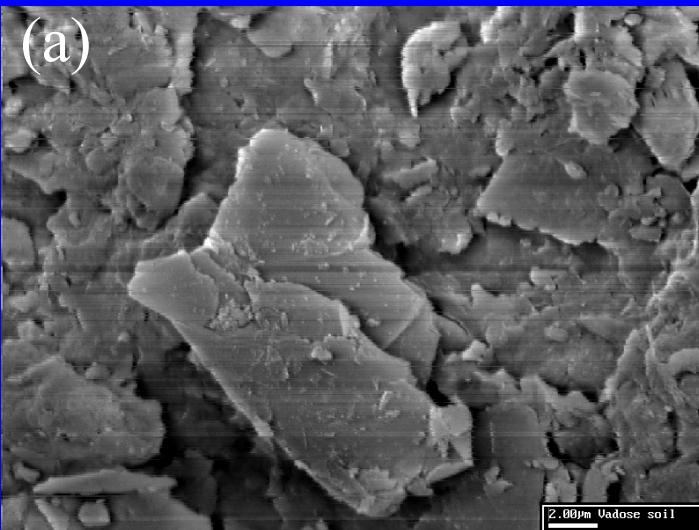
Agricultural Soils

Yolo Vadose (a)

0.32% OC

Yolo Surface (b)

1.2% OC



Forest Soils

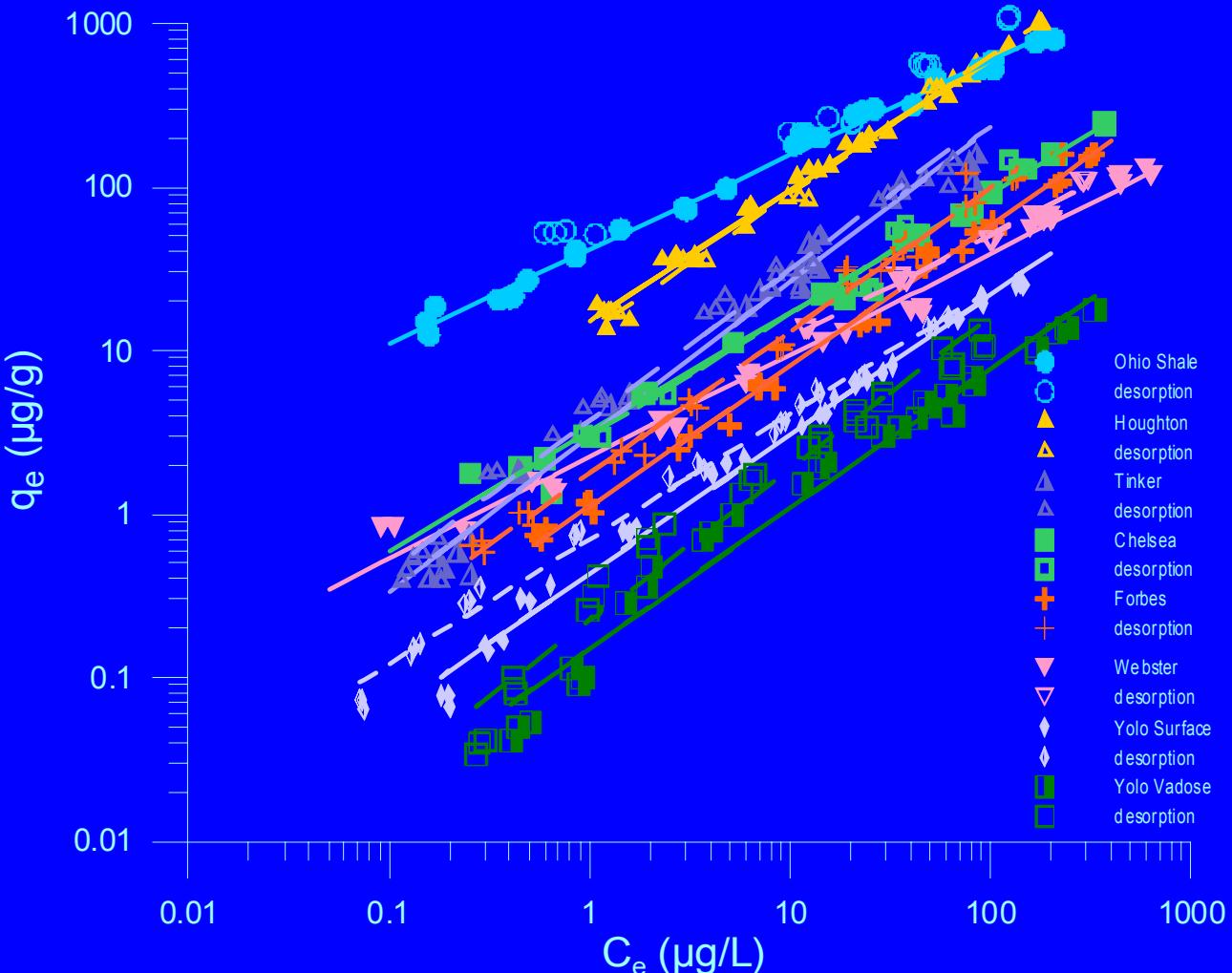
Forbes (c)

4.30% OC

Tinker (d)

11.0% OC

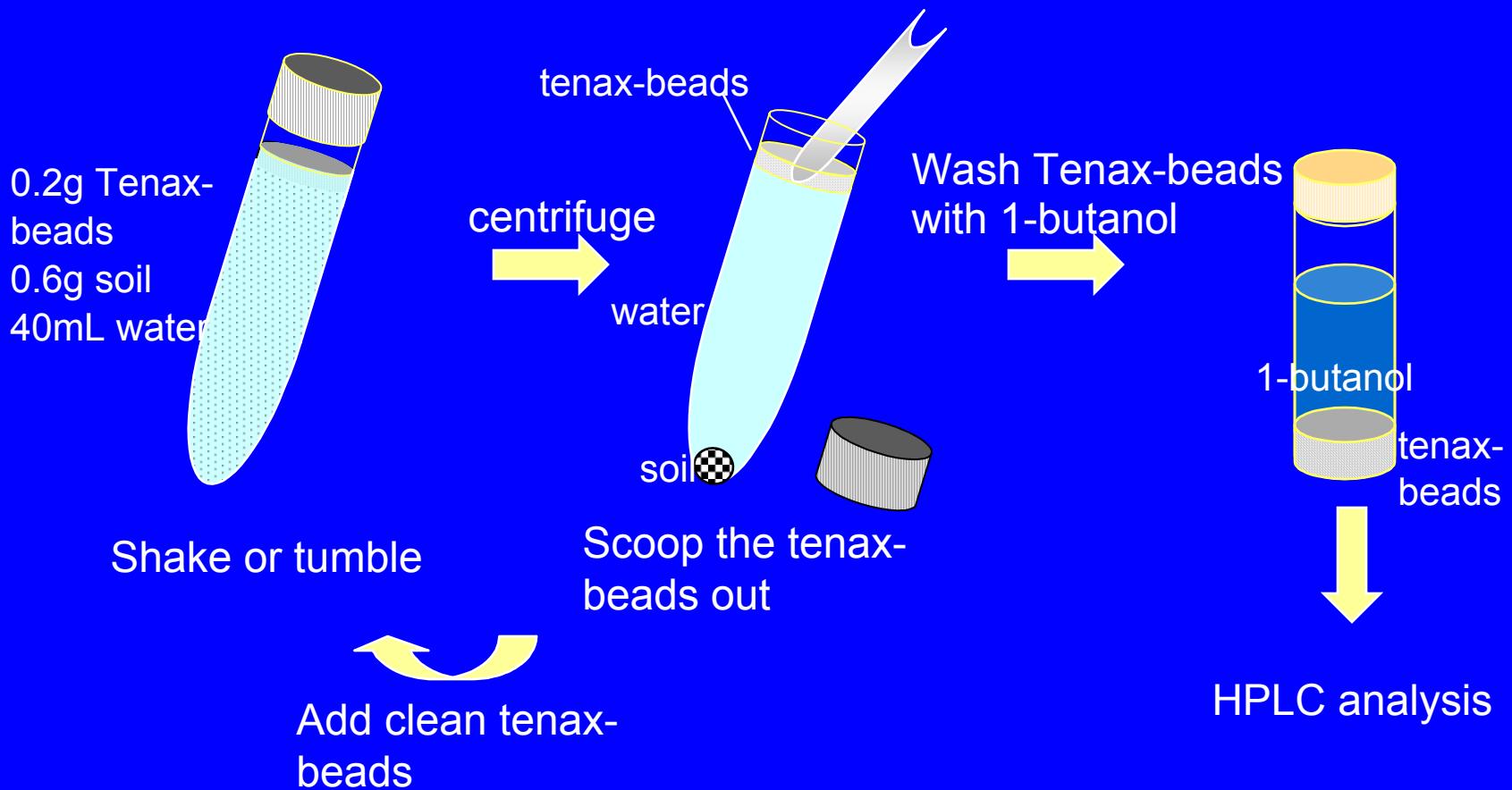
Isotherm study



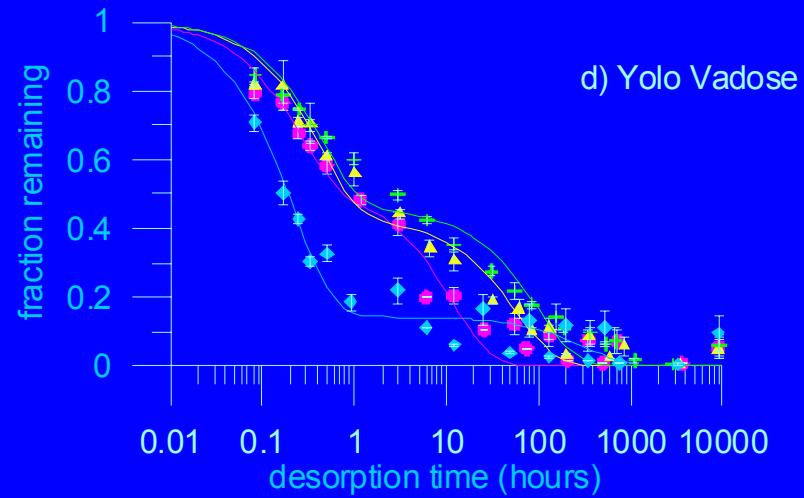
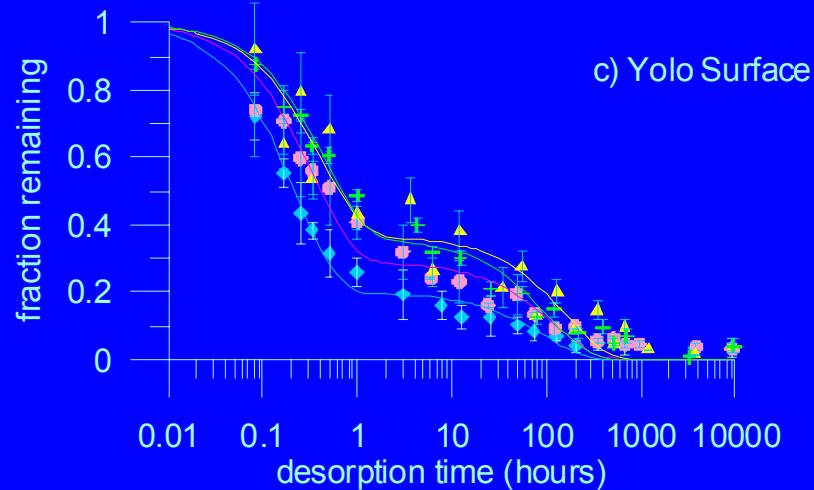
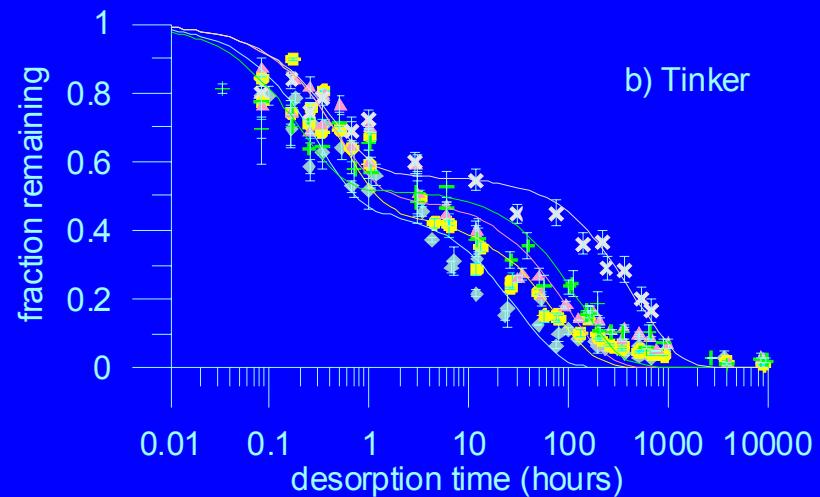
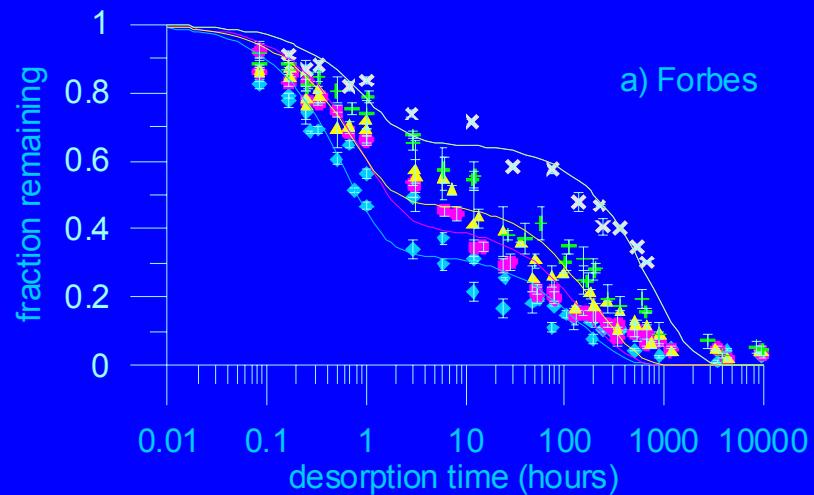
Hysteresis Index

$$HI = \left. \frac{q_e^d - q_e^s}{q_e^s} \right|_{T, C_e}$$

Desorption Rate Methodology

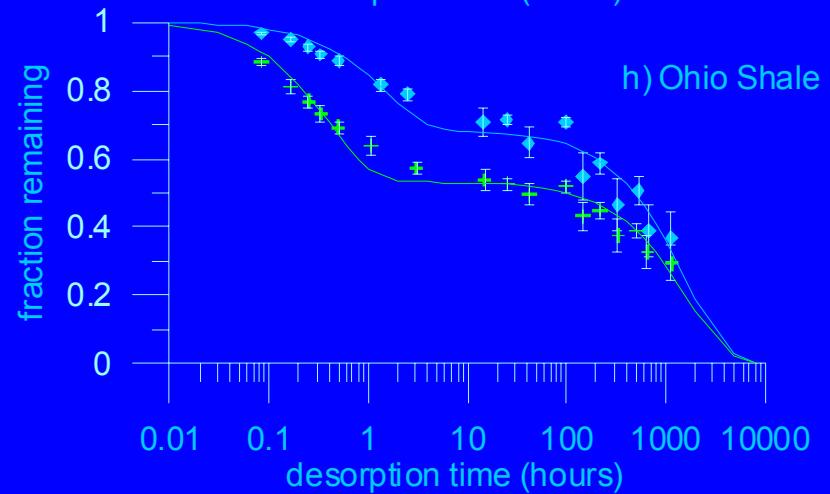
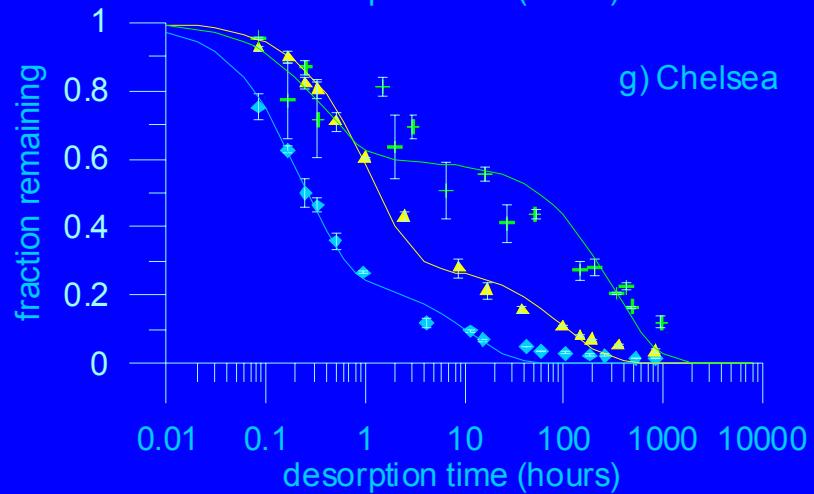
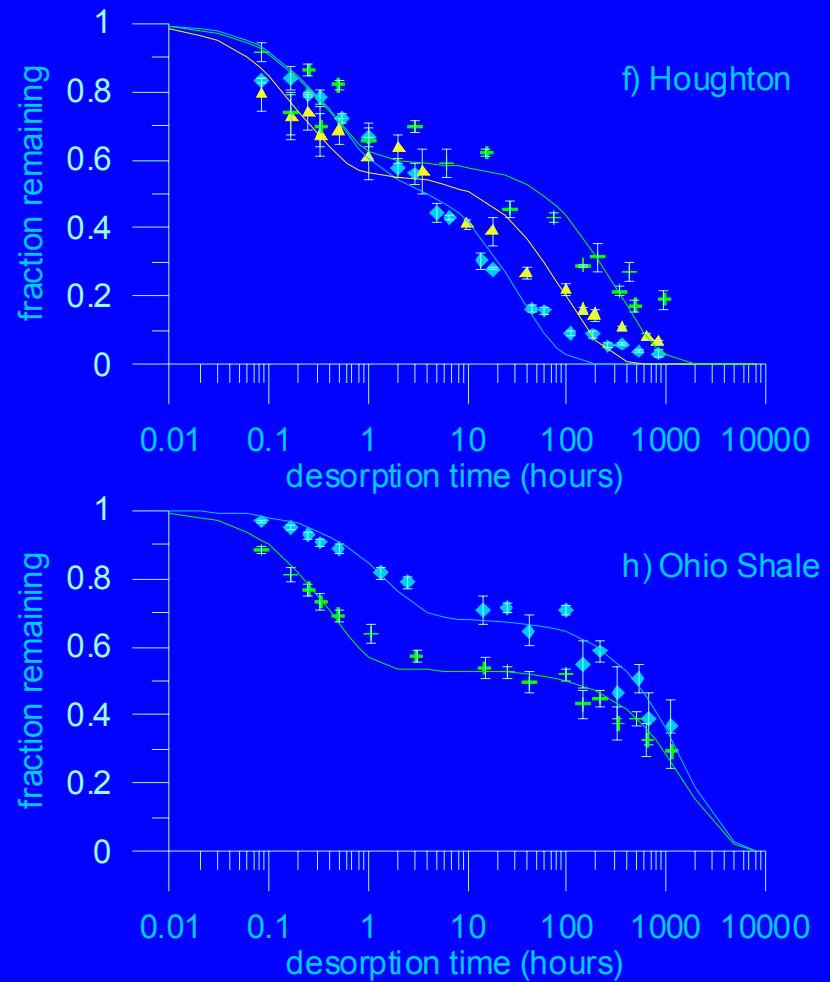
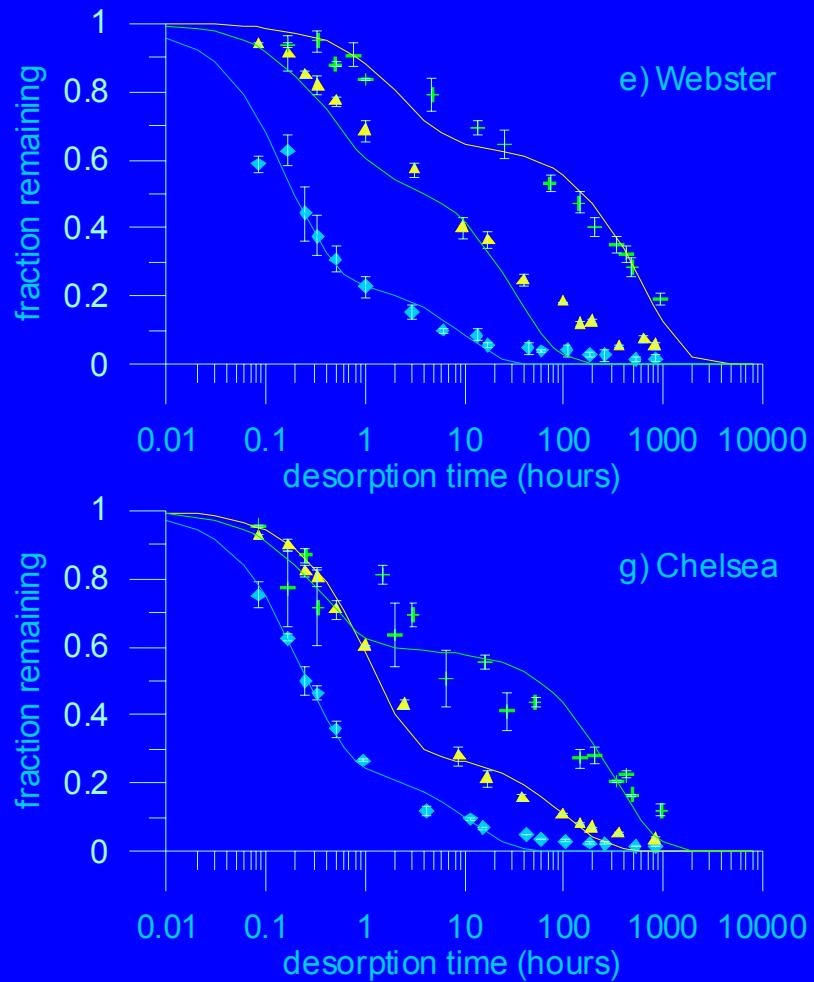


Desorption Rate Results



Aging time : □ 1h, ● 1d, ▲ 1w, + 1m, ✕ 18m

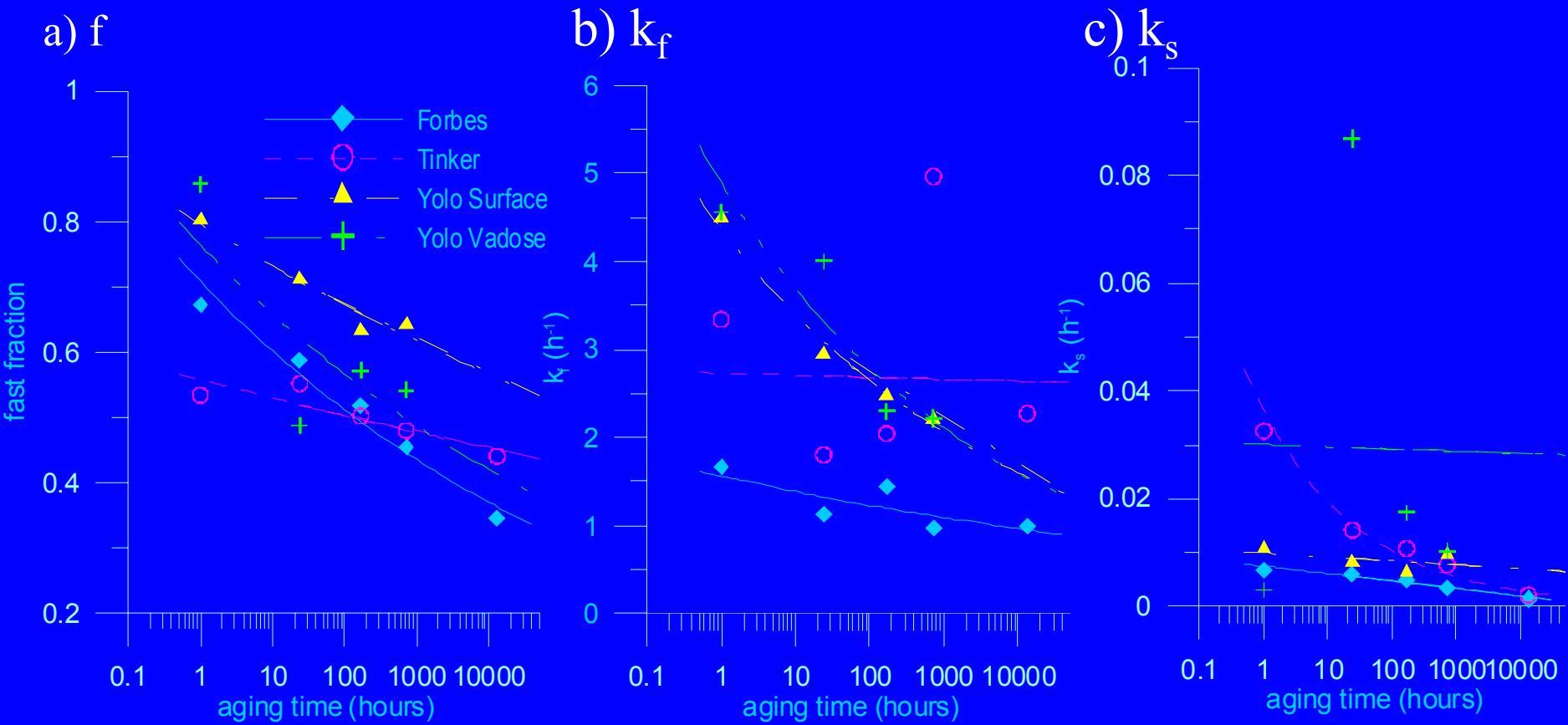
Desorption Rate Results (2)



Aging time : □ 1h, ▲ 1w, + 1m

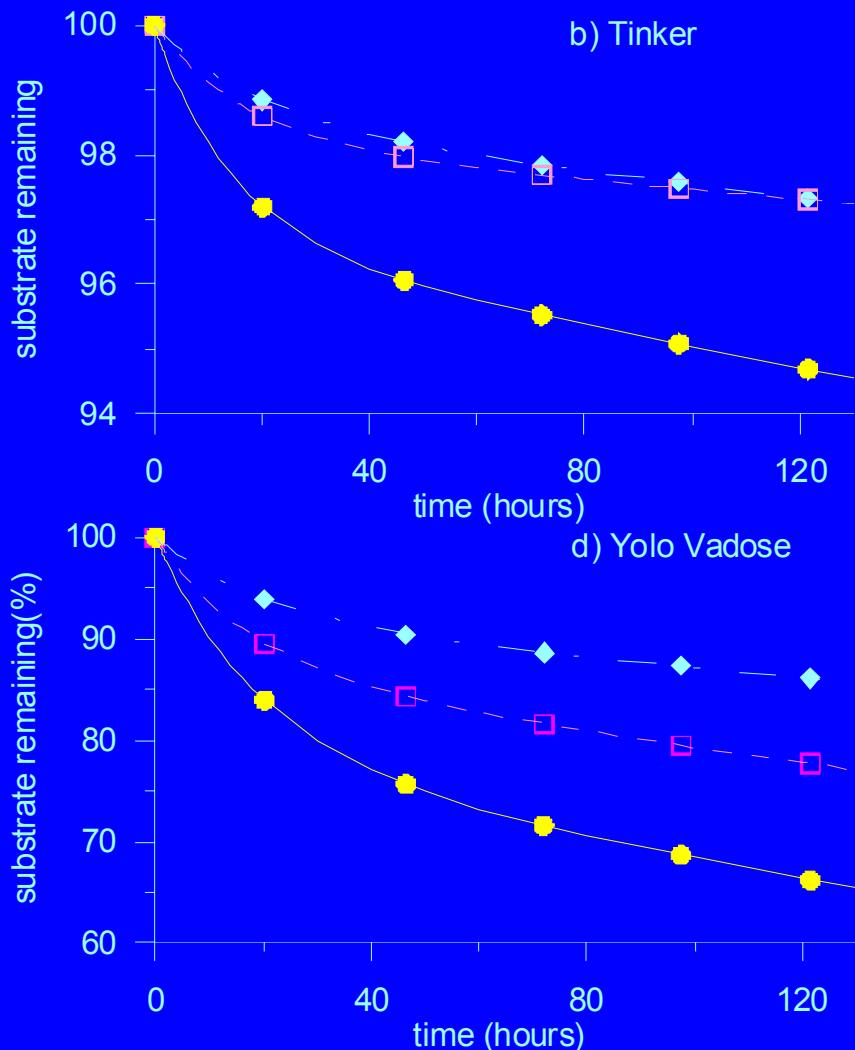
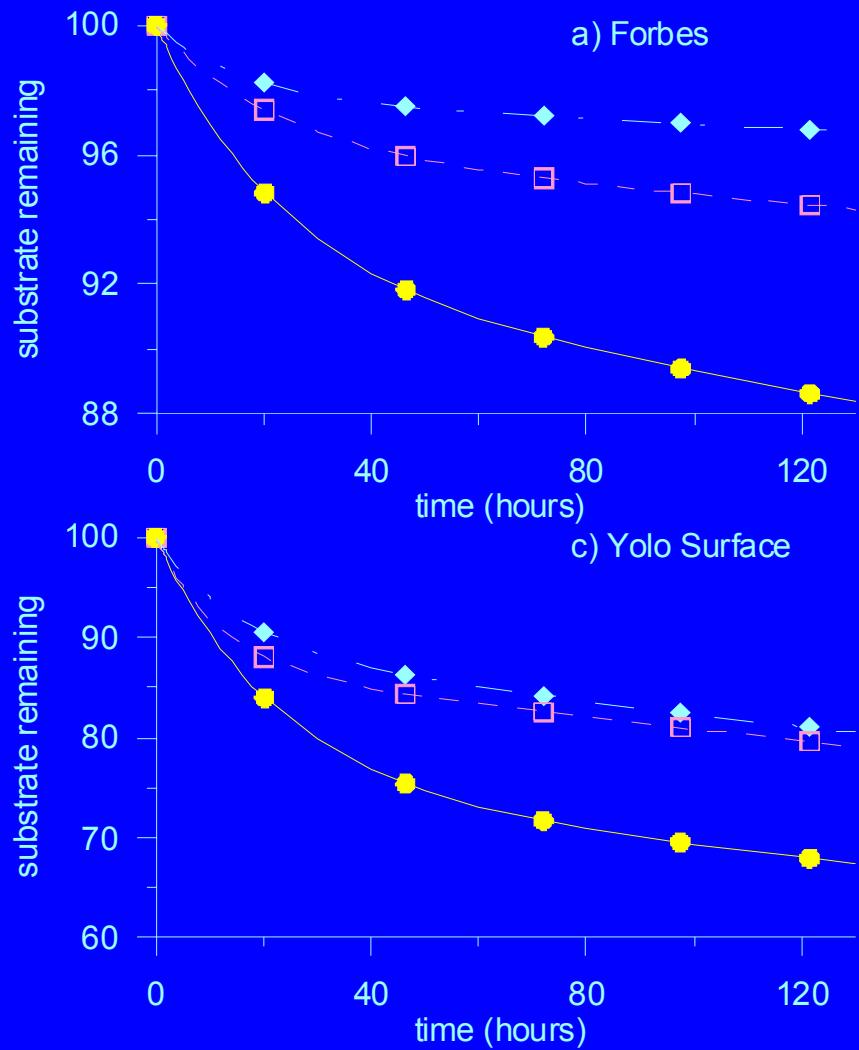
Two-site Model Parameters-Desorption

$$F = f \exp(-k_f t) + (1-f) \exp(-k_s t)$$



Mineralization Study

two-site model fits

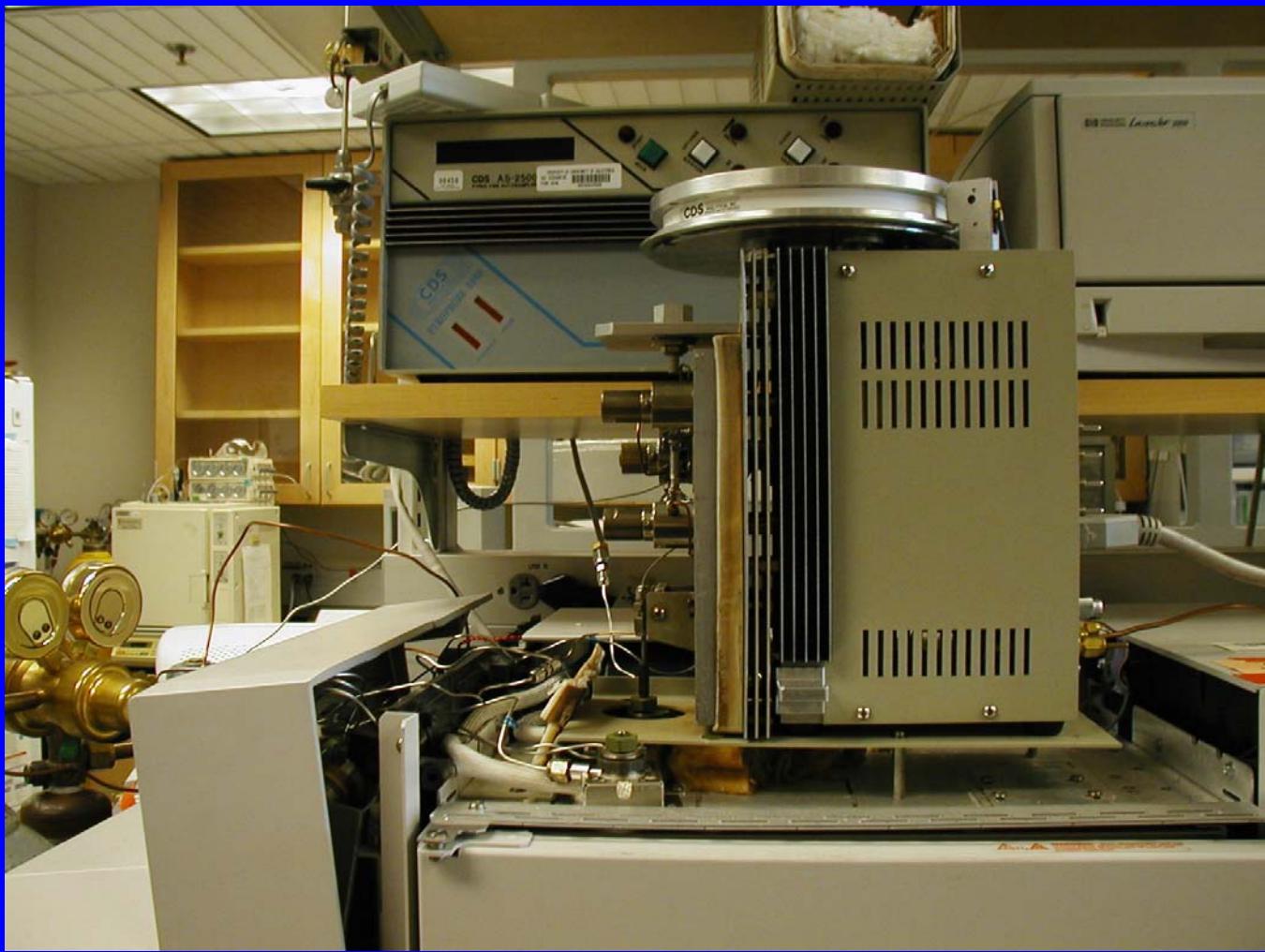


♦ :24 hours, □ :168 hours, ● :600 hours of aging

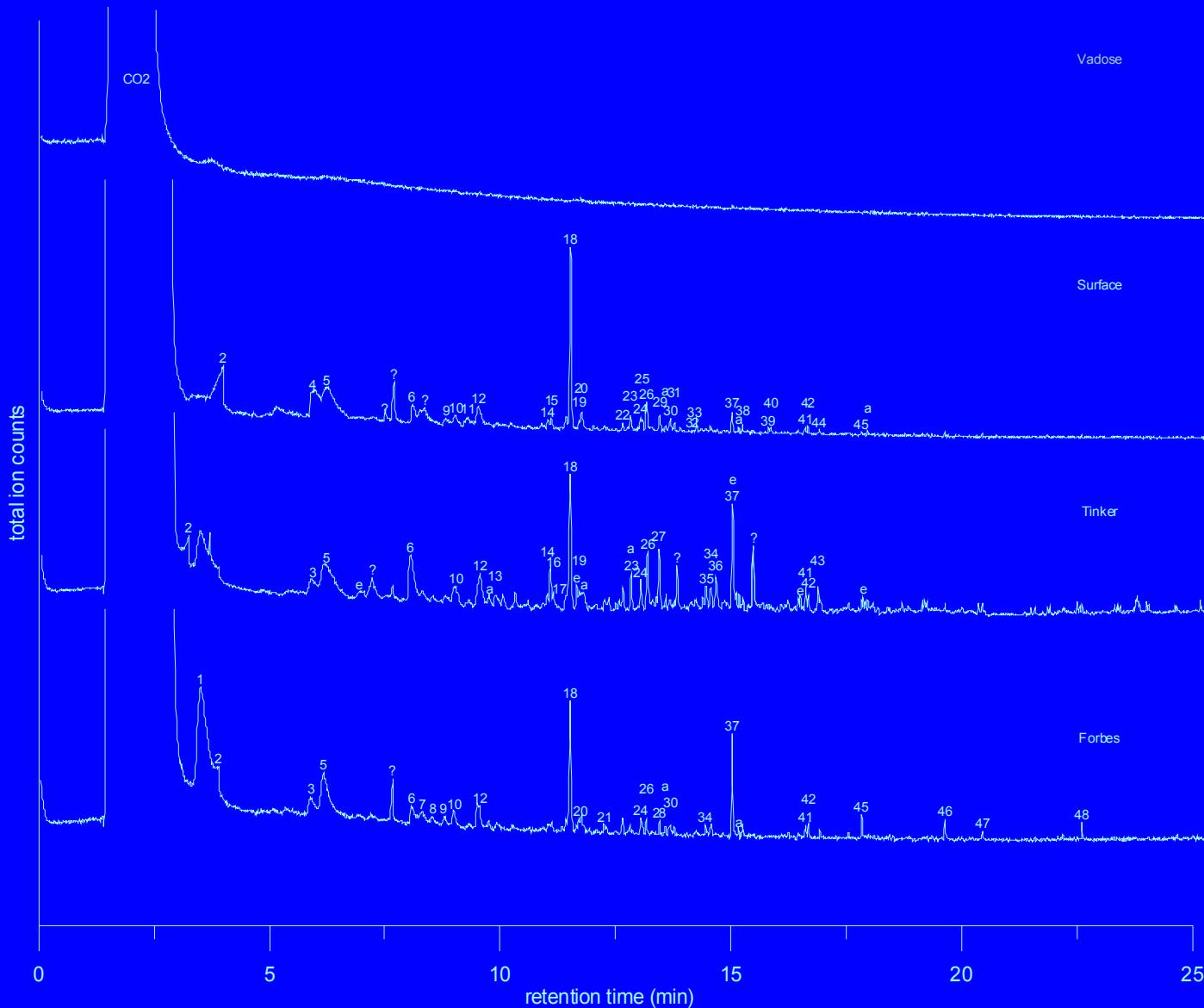
Study Design--NMR and Pyrolysis

- Pyrolysis GC-MS on whole soils
 - 650 °C for 30s in He (10°C ms⁻¹)
 - CDS pyroprobe 2500
- Solid state CP-MAS ¹³C NMR
 - Chemagnetics CMX-400 Infinity at 100.6 MHz for ¹³C
 - 20,000 to 40,000 acquisitions, 1s relaxation delay, 1ms contact time, 4.5 kHz spinning rate
 - Samples demineralized with HF prior to analysis

Pyrolysis GC/MS



Pyrograms



1benzene
2acetic acid
3pyrrole
4pyridine
5toluene
5toluene
6furfural
72-methyl-1H-pyrrole
83-methyl-1H-pyrrole
9ethylbenzene
10xylene
11aniline
12styrene/xylene
132-methyl-2-cyclopenten-1-one
14benzaldehyde
155-methylfurfural
163-methyl-2-cyclopenten-1-one
175-methylfurfural
18phenol/benzonitrile
191,2,4-trimethylbenzene
20benzfuran
211,2,3-trimethylbenzene
22indene
232-methylphenol
24acetophenone
25o-tolunitrile
264-methylphenol
272-methoxyphenol
28o-tolunitrile
29m-tolunitrile
30p-tolunitrile
312-methylbenzfuran
322-methylbenzoxazole
33benzyl nitrile
342-methylindene
353-methyl-1H-indene
364-ethylphenol
37naphthalene
382-nonen-1-ol, {E}-
39benzylacetonitrile
40isoquinoline
41indole
422-methylnaphthalene
432-methoxy-4-vinylphenol
441-methylnaphthalene
45biphenyl
46dibenzofuran
47fluorene
48phenanthrene
aalkane
ealkene

Pyrolysis GC/MS – Results (1)

	Pyrolysis recovery (%) ^a	OC recovery (%) ^b	OC recovery w/o CO ₂ (%) ^c	N recovery (%) ^d
Tinker	46.9 (9.3)	69.4 (4.8)	4.9 (0.2)	11.1 (1.8)
Forbes	83.1 (2.6)	92.3 (1.7)	5.1 (1.4)	22.1 (2.9)
Yolo Surface	98.6 (5.2)	65.6 (20.1)	3.3 (1.1)	9.13 (2.6)
Yolo Vadose	133.8 (11.9)	75.3 (7.1)	1.50 (0.4)	3.48 (0.4)
Houghton	65.6 (5.0)	38.7 (0.7)	6.2 (0.4)	65.0 (54.8)
Chelsea	84.7 (9.5)	58.8 (7.0)	6.0 (0.4)	18.8 (1.0)
Webster	94.1 (20.0)	57.8 (25.9)	4.9 (2.3)	17.4 (6.2)
Ohio Shale	68.5 (10.7)	19.7 (7.7)	7.3 (3.0)	-

a) (amount pyrolyzed (μg)) / (OM content (μg)) x 100%

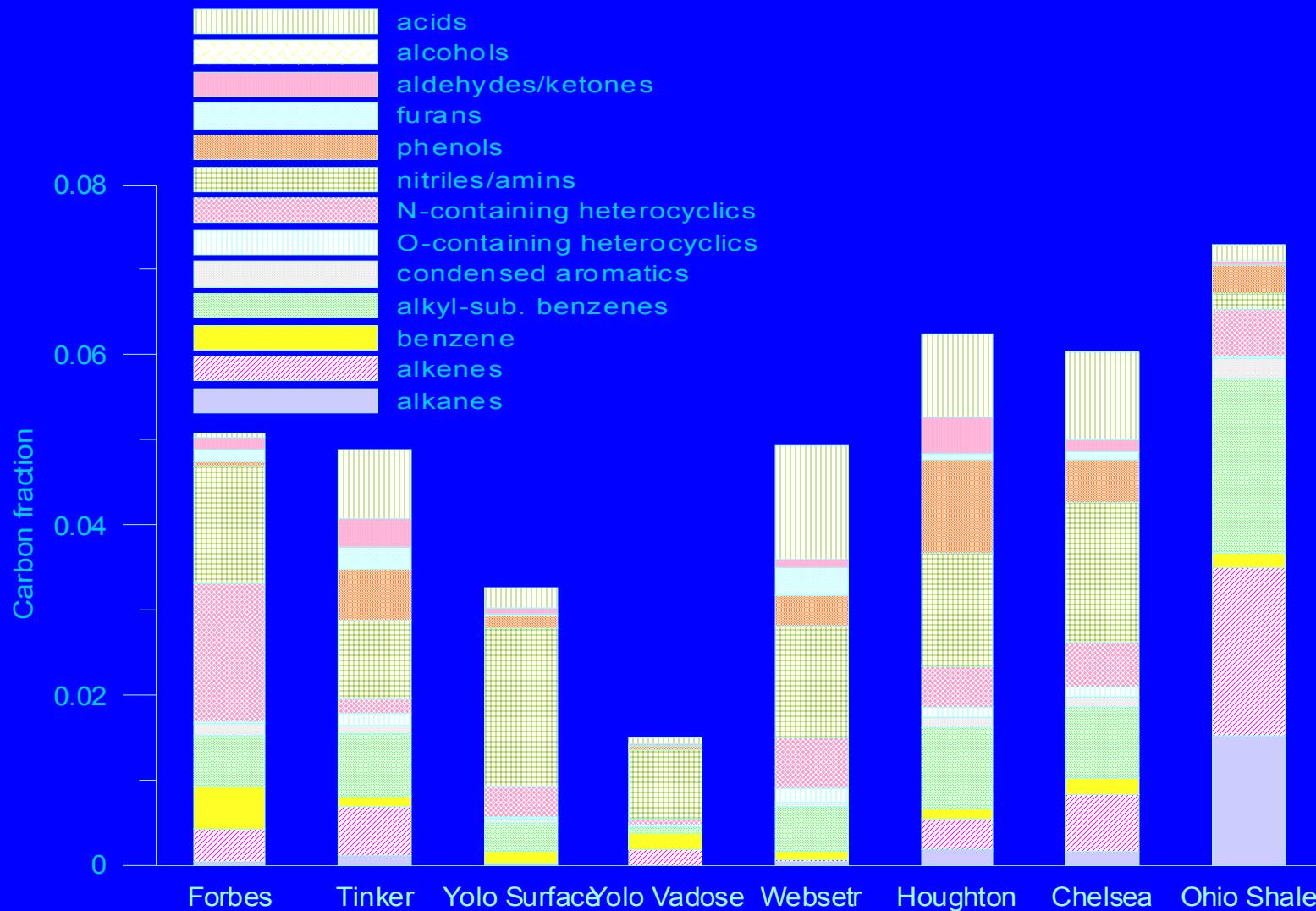
b) $\frac{\sum \{(\text{moles of compound quantified (moles)}) \times (\text{number of carbon in each compound})\}}{\text{number of carbon pyrolyzed}} \times 100\%$

c) b – number of carbon recovered as CO₂

d) $\frac{\sum \{(\text{moles of compound quantified (moles)}) \times (\text{number of nitrogen in each compound})\}}{\text{number of nitrogen pyrolyzed}} \times 100\%$

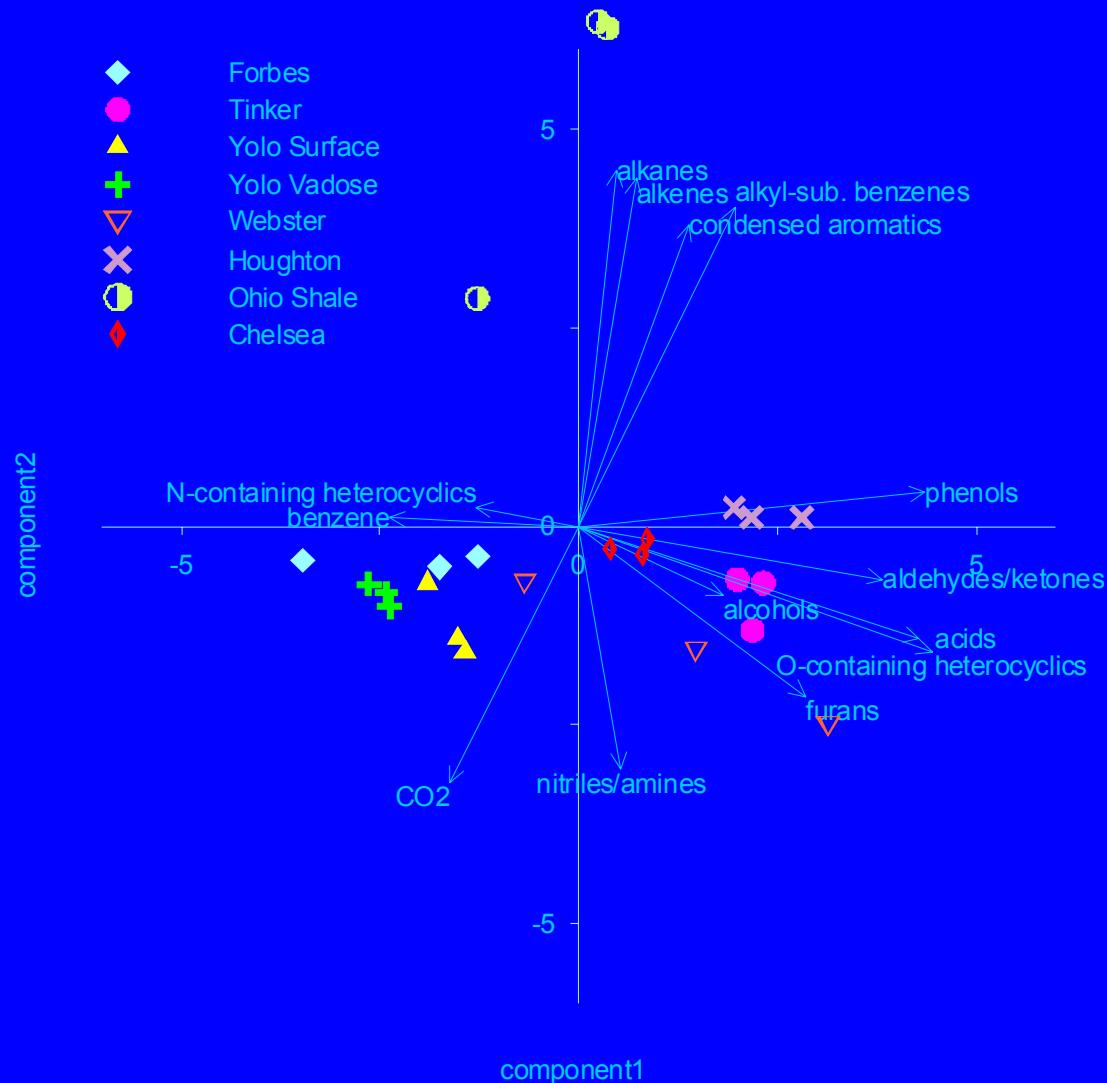
Pyrolysis GC/MS – Results (2)

Major functional groups

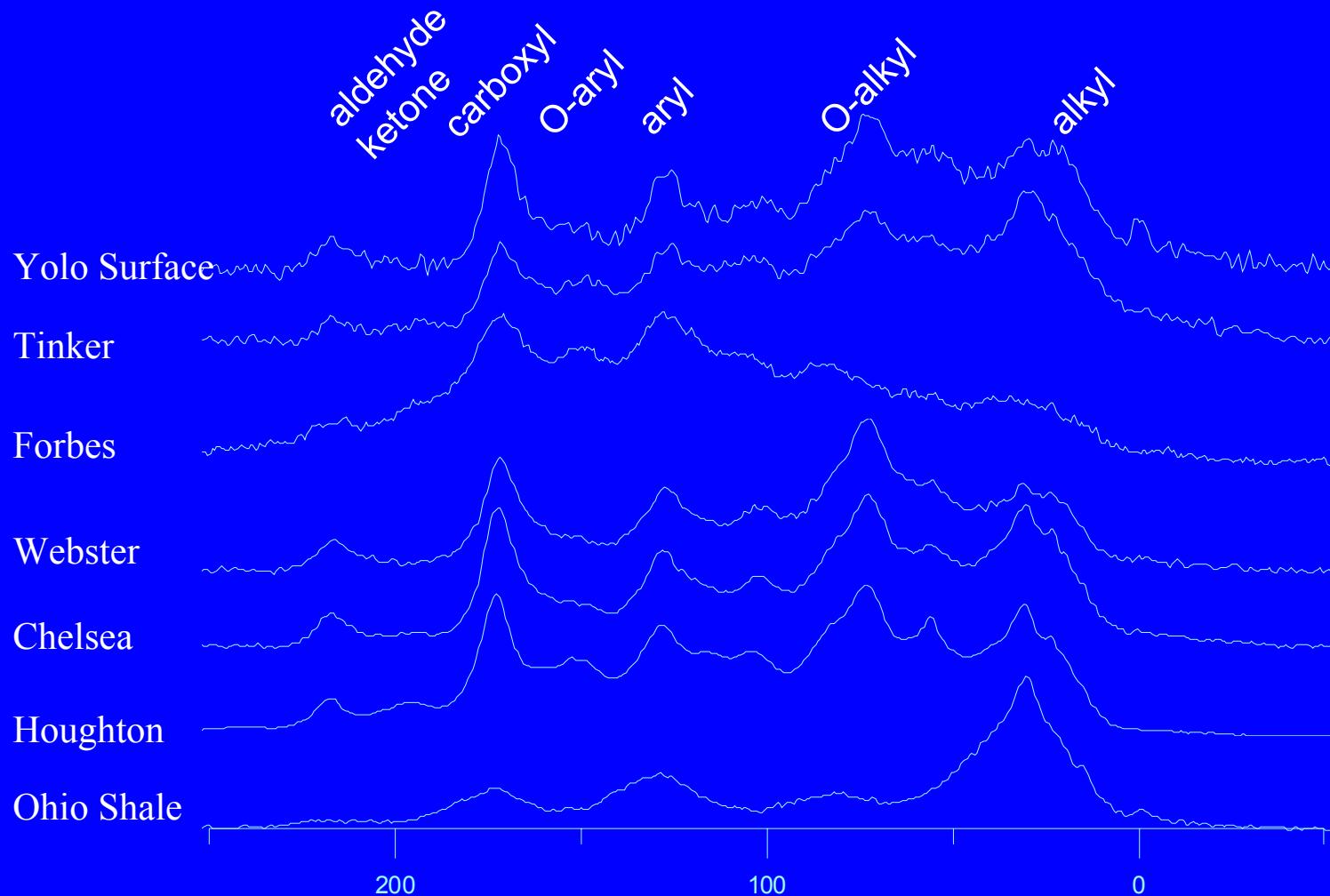


Pyrolysis GC/MS – Results (3)

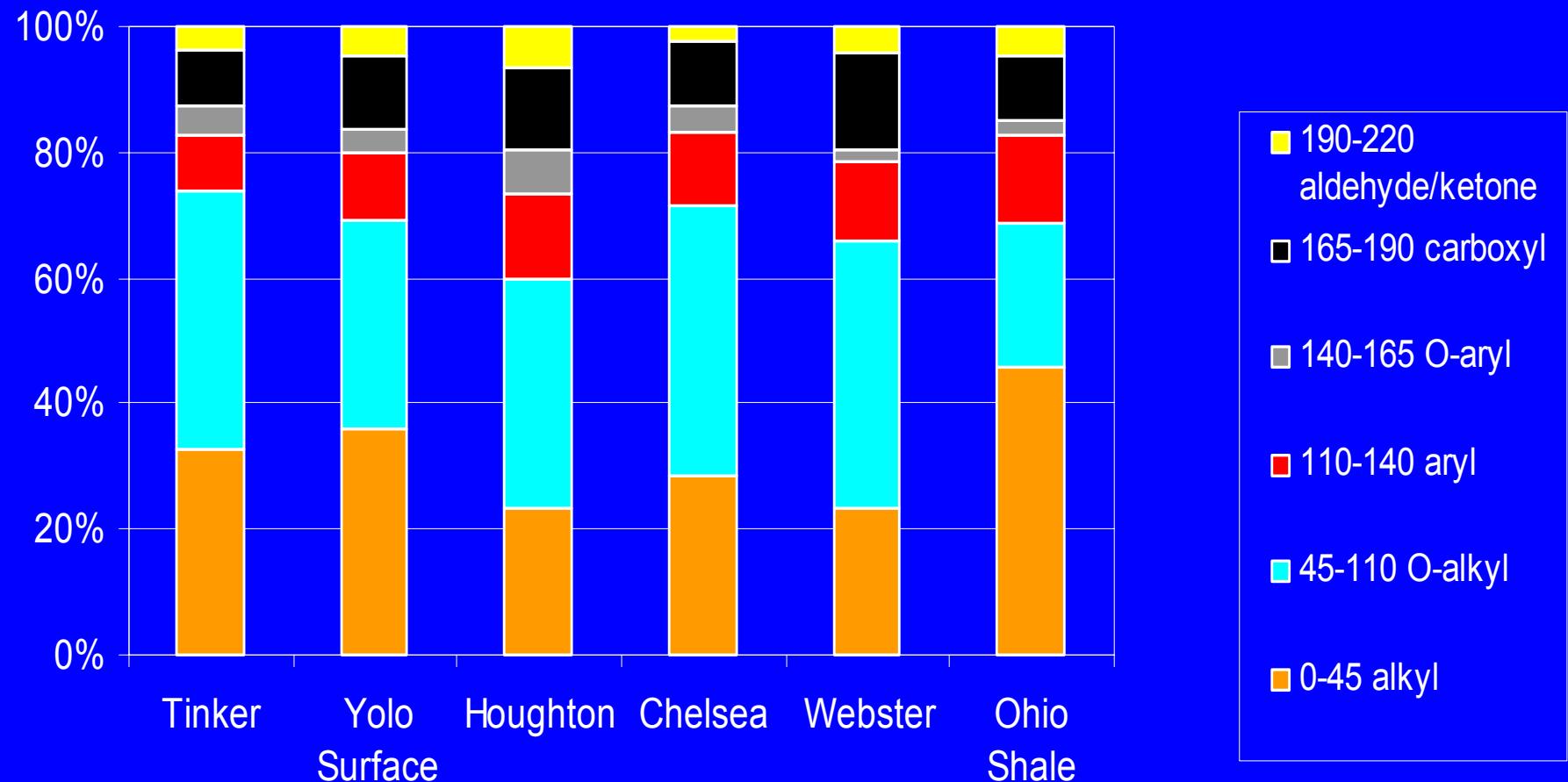
principal component analysis 8 geosorbents



NMR Spectra

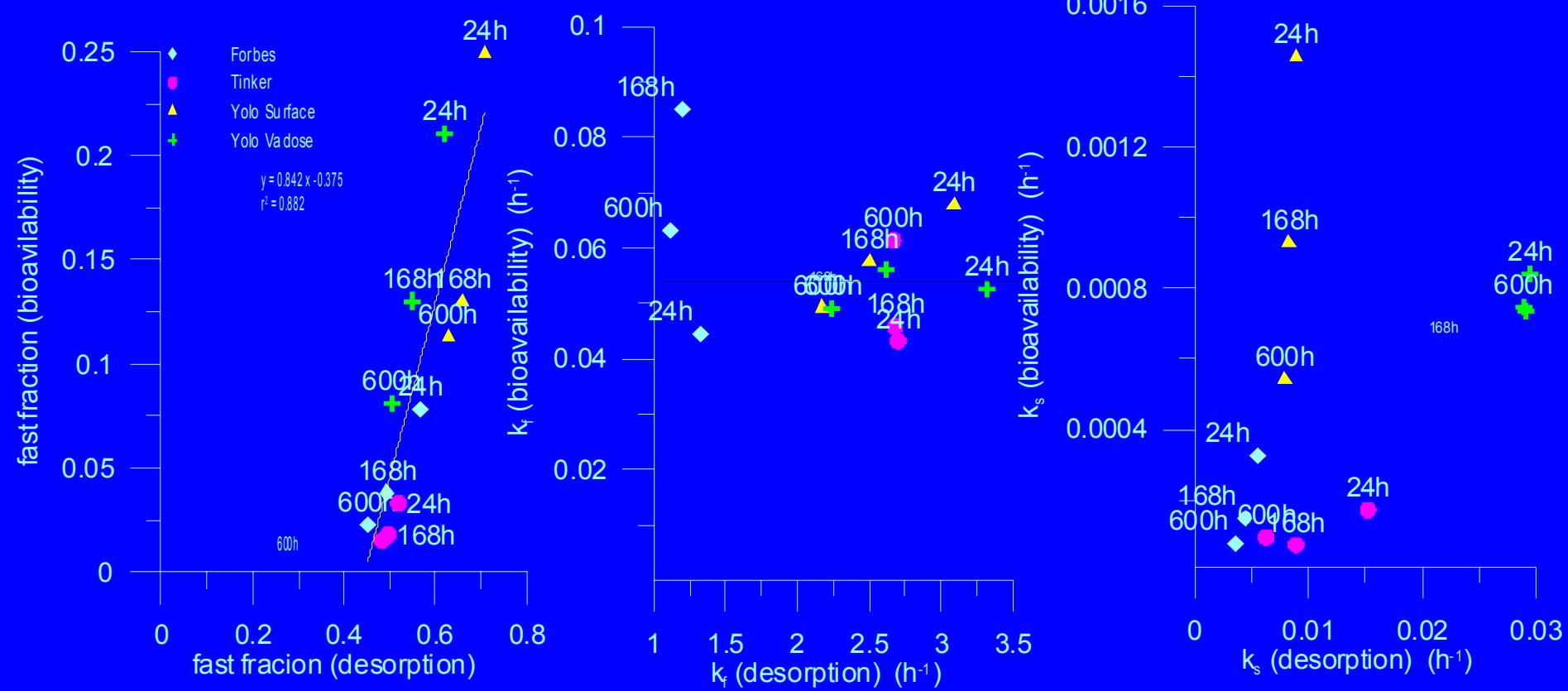


¹³C NMR Integration Results

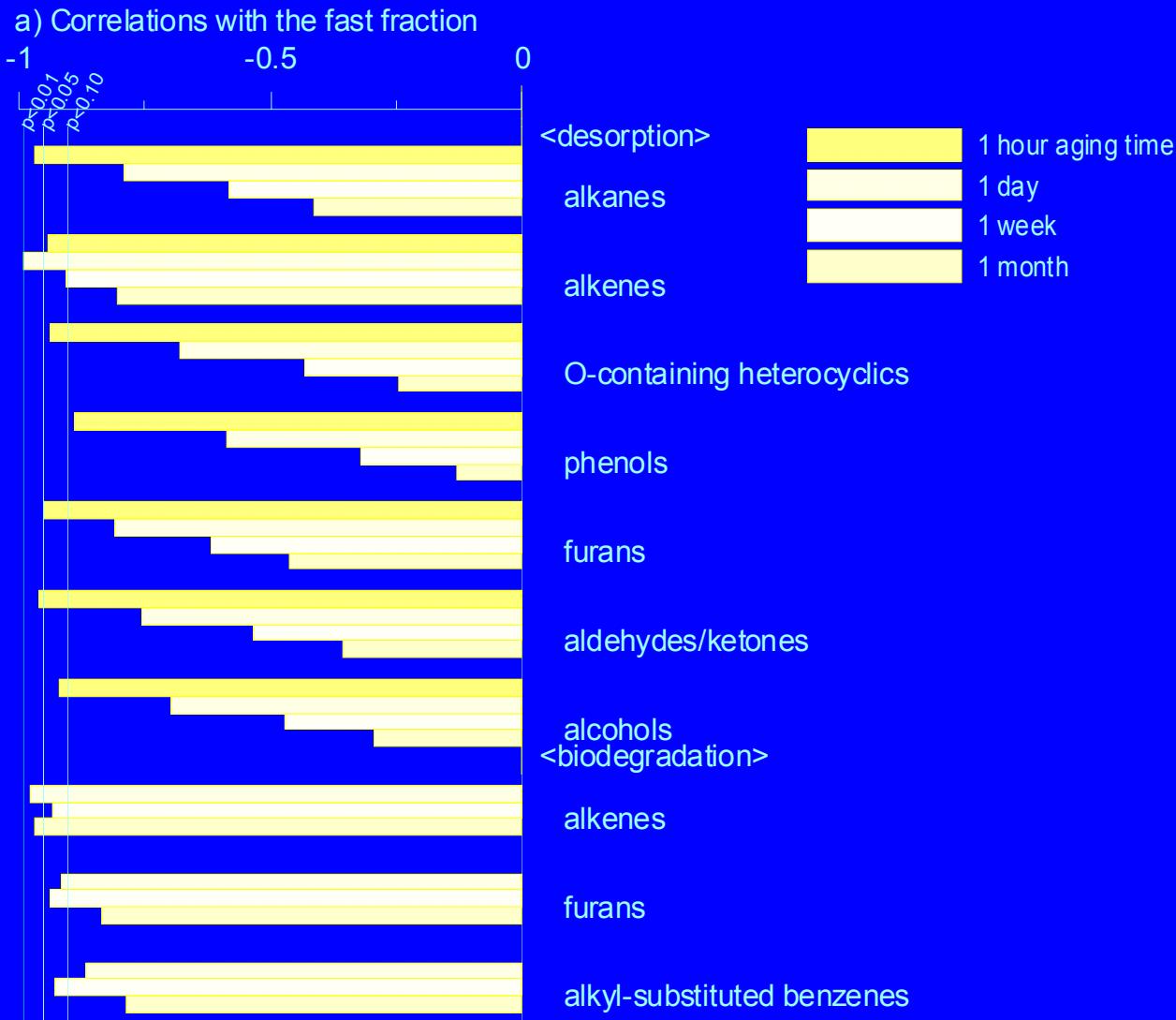


Does desorption control biodegradation?

Comparison of two-site model parameters

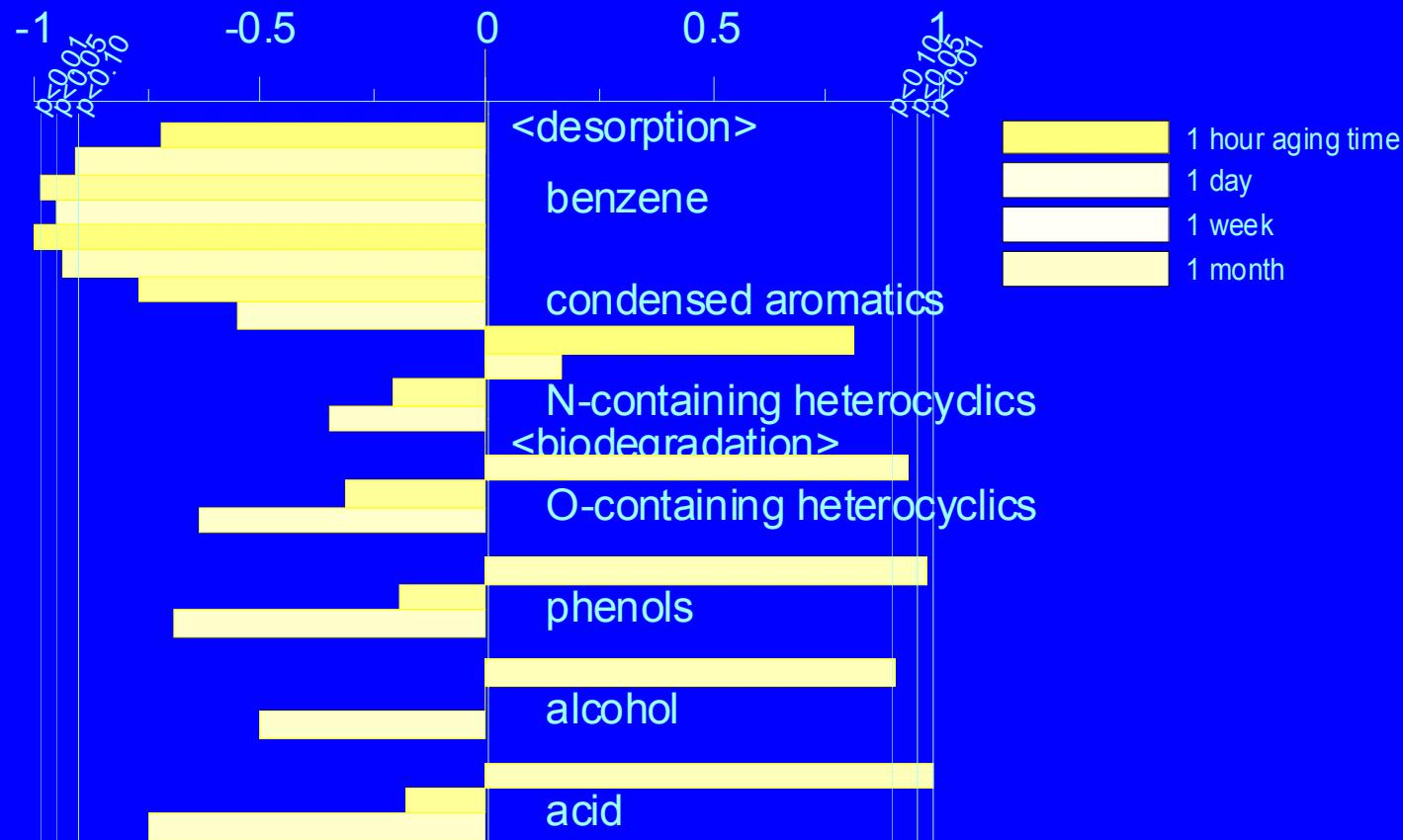


SOM Structures Controlling Desorption and Biodegradation

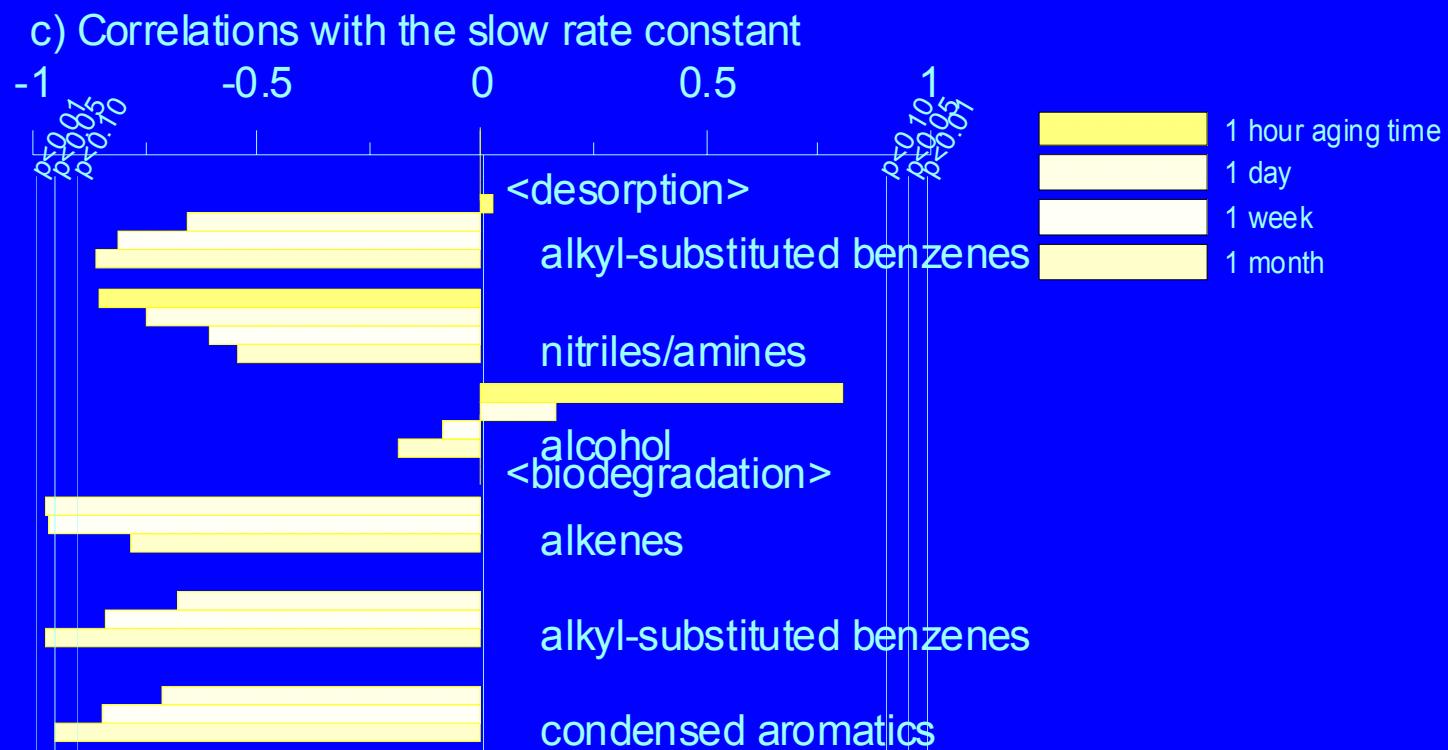


SOM Structures Controlling Desorption and Biodegradation (2)

b) Correlations with the fast rate constant



SOM Structures Controlling Desorption and Biodegradation (3)



Pyrolysis and NMR Results--Correlations

¹³C NMR peak group	Pyrolysis GC-MS peak group
Aldehyde/ketone C	Benzene (+++) N-containing heterocyclics (+++)
Carboxyl C	Benzene (+) N-containing heterocyclics (+++)
O-aryl C	Benzene (++) N-containing heterocyclics (+)
Aryl C	Benzene (++) N-containing heterocyclics (+++)
O-alkyl C	Alkanes (--) Alkenes (--) Alkyl benzenes (--) Condensed aromatics (---)
Alkyl C	CO ₂ (-) Alkanes (++) Alkenes (++) Alkyl benzenes (+)

Conclusions

- Support for the idea that desorption resistance controls biodegradation, at least for slower, long-term component
- Relation between sorption properties and SOM structure
 - K_{OC} and HI – no significant correlations with any pyrolysis peaks, but with free iron, aluminum, amorphous iron (Koc of desorption) and amorphous aluminum (HI).
 - negative correlations between f and alkanes, alkenes and O-containing groups, decreasing with aging time.
 - negative correlations between k_s and alkyl substituted benzenes, condensed aromatics, increasing with aging time.
- Establishing a structure-function relationship in this area is clearly challenging but justified by the benefits of mechanistic understanding

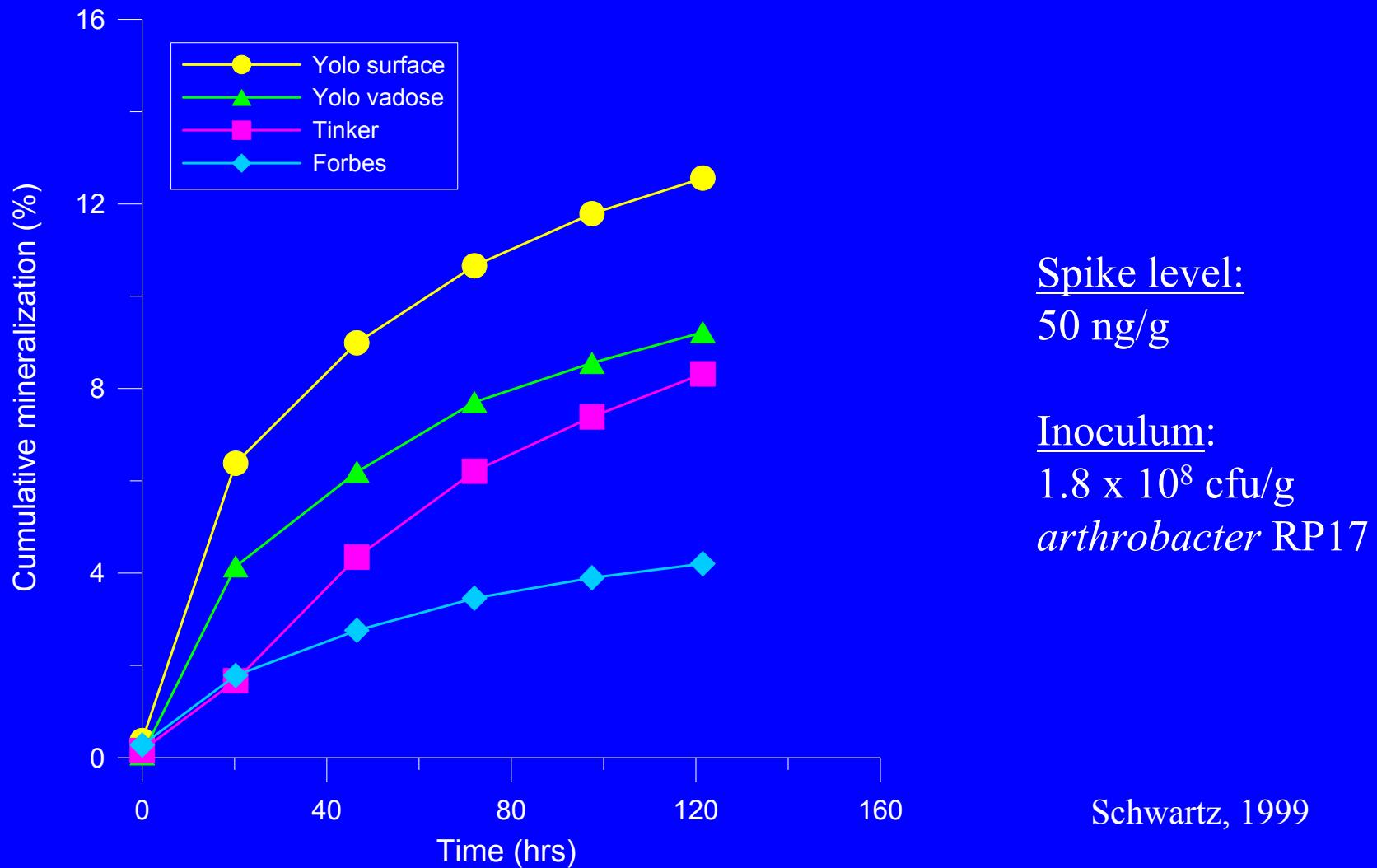
Acknowledgments

- Naoko Watanabe, desorption rate, pyrolysis, and NMR data
- Daeyoung Ju, competitive sorption/desorption data
- Egbert Schwartz, biodegradation data
- Brian Philips, ^{13}C NMR assistance
- Funding from the Department of Energy, the National Science Foundation, and NIEHS

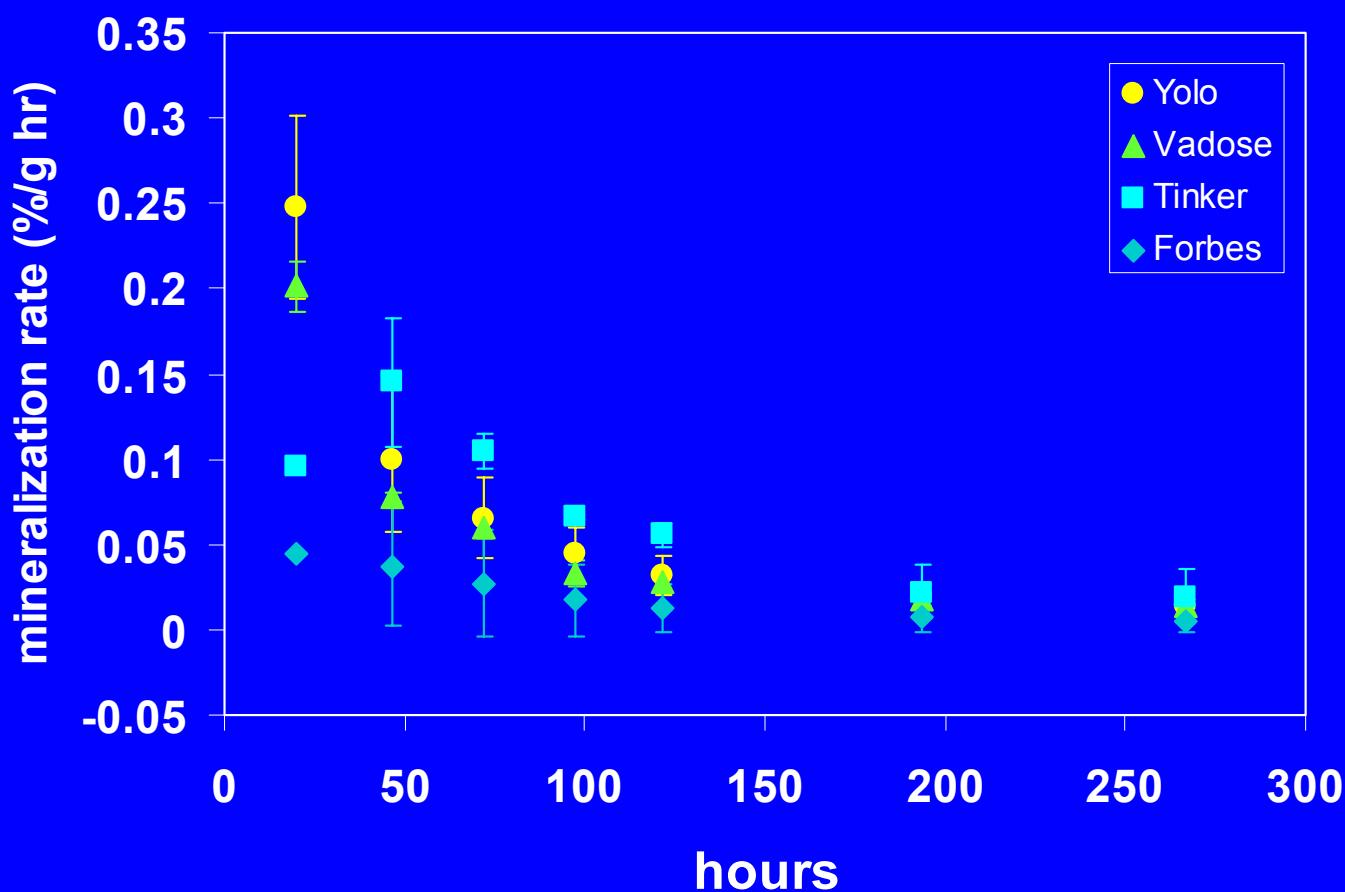
Pyrolysis GC/MS -- Major Peaks

Pyrolysis compound	Origin	Carbon fraction ($\times 10^5$)			
		Forbes	Tinker	Yolo Surface	Yolo Vadose
alkanes	Alkane ¹⁾	40.4(23.4)	104.7(14.0)		
alkenes	Alkane ¹⁾		569.4(84.9)		
acetaldehyde	Carbohydrate	72.5(13.2)		35.8(4.0)	
cyclopentene	Carbohydrate	384.1(140.7)			189.2(37.7)
2-methylfuran	Carbohydrate ^{1?)}	80.4(34.5)	135.7(26.1)		
acetic acid	Carbohydrate ¹⁾	62.9(3.7)	730.1(28.0)	246.3(109.2)	73.5(52.5)
hydroxyacetone	Carbohydrate		102.7(17.6)		4.0(6.9)
2-furaldehyde	Carbohydrate ¹⁾		99.9(7.6)	19.9(9.4)	3.4(2.4)
2-methyl-2-cyclopenten-1-one	Carbohydrate ¹⁾		38.6(3.4)		
5-methylfurfural	Carbohydrate ¹⁾	53.4(20.4)	139.3(13.8)	37.8(13.1)	
acetophenone	Carbohydrate		49.5(6.6)		
naphthalene	Carbohydrate	56.5(3.4)	15.6(7.9)		10.3(2.1)
tetradecanoic acid	Carbohydrate				2.6(4.6)
biphenyl	Carbohydrate				3.3(1.2)
benzene	Carbohydrate/protein	499.5(261.8)	134.1(31.7)	145.1(66.2)	190.9(30.7)
styrene	Carbohydrate/protein	38.6(23.8)		19.1(8.6)	4.3(1.8)
2-methoxy-4-vinyl phenol	Lignin ^{1?)}		44.6(26.7)		36.2(38.6)
phenol	Lignin + protein ¹⁾		147.9(28.4)	84.4(42.7)	3.3(3.0)
2-methylphenol	Lignin + protein ¹⁾		50.6(15.4)		
4-methylphenol	Lignin + protein ¹⁾		63.6(12.4)		
2,4-dimethylphenol	Lignin + protein ¹⁾		64.4(11.6)		2.8(2.6)
3-ethylphenol	Lignin + protein ^{1?)}		147.0(13.2)		
2-propenenitrile	Protein	84.7(56.4)			110.7(27.1)
acetonitrile	Protein	1155.3(225.2)	730.2(111.2)	1615.8(506.0)	577.6(30.7)
benzonitrile	Protein ¹⁾	87.1(17.9)	55.5(15.8)	130.6(40.4)	116.0(27.5)
phenylacetonitrile	Protein ²⁾	25.9(11.6)	51.8(5.6)	42.0(16.1)	4.1(3.7)
benzylacetonitrile	Protein ²⁾			17.0(6.9)	
indole	Protein ²⁾				6.1(10.6)
1H-pyrrole, 2-methyl-	Protein ²⁾	40.9(5.9)		53.2(4.6)	
2-methylbenzoxazole	Protein ²⁾			16.9(1.1)	
3-methylpyrrole	Protein ²⁾	38.5(6.6)		53.2(4.6)	
3-picoline	Protein ²⁾	28.3(7.4)		45.0(2.9)	
isoquinoline	Protein ²⁾	1296.9(1758.3)			
methylpyrrole	Protein ²⁾	41.0(10.4)		54.0(4.7)	
m-tolunitrile	Protein ²⁾			38.8(15.1)	5.1(5.0)
pyridine	Protein ²⁾	34.7(24.2)		46.2(3.9)	23.5(22.8)
pyrrole	Protein ²⁾	91.9(27.6)	44.0(12.6)	65.7(10.1)	50.7(49.6)

Cumulative Mineralization

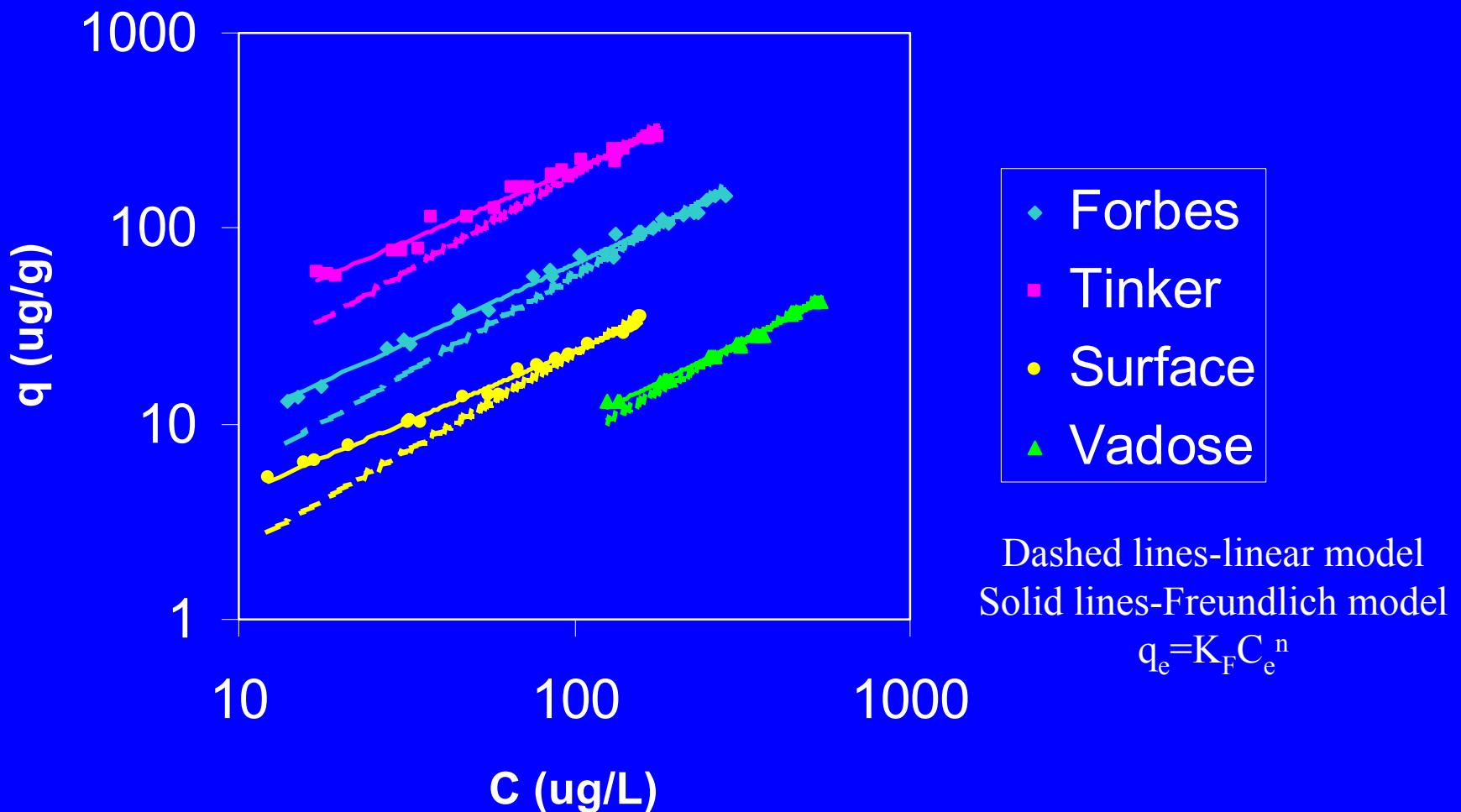


Mineralization rates after 600 hrs aging



Inoculum:
 $1.2 \times 10^8 \text{ cfu/g}$
arthrobacter RP17

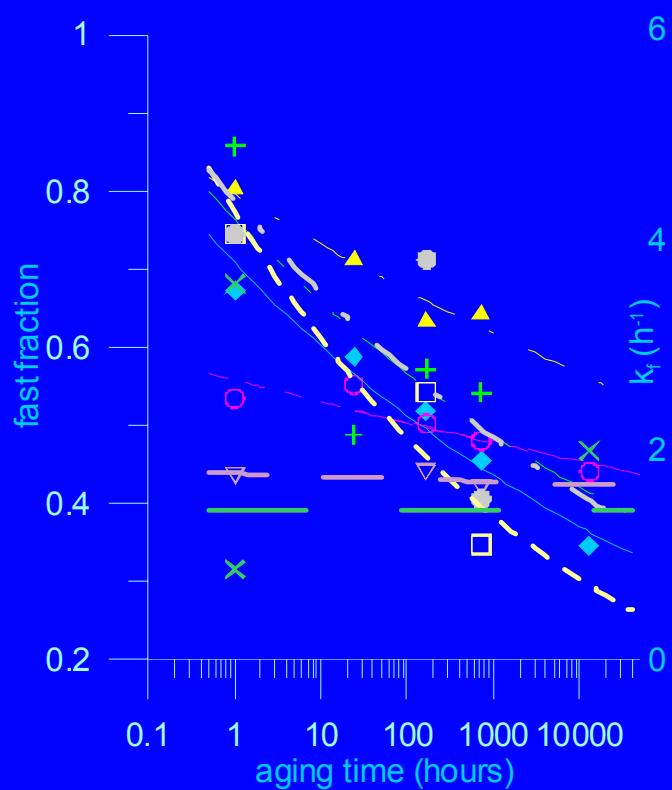
Sorption Isotherms: Logarithmic View



Two-site Model Parameters- Full Set

$$F = f \exp(-k_f t) + (1-f) \exp(-k_s t)$$

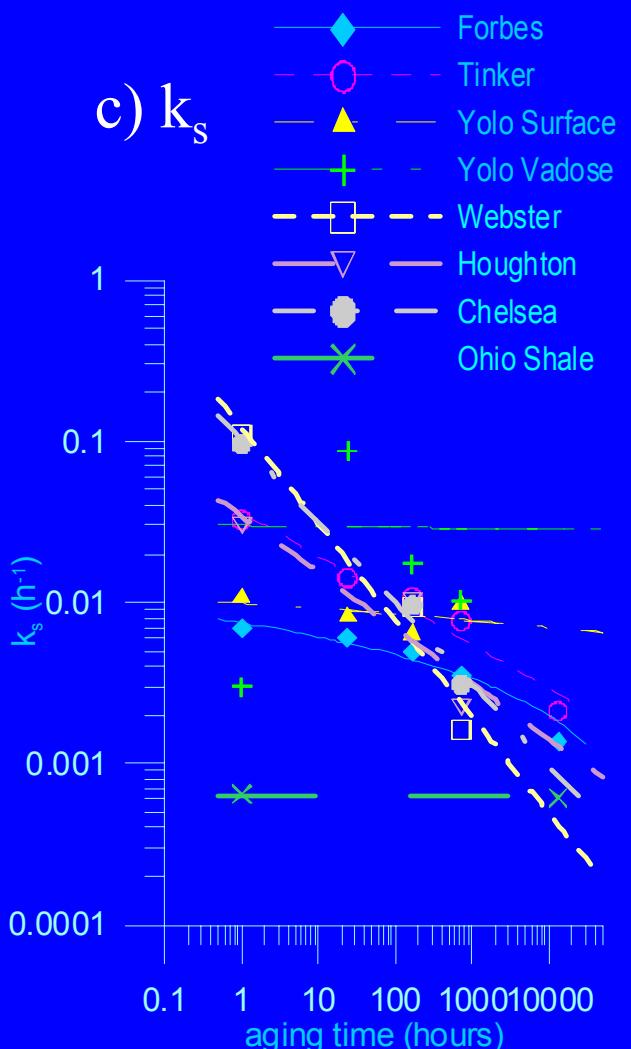
a) f



b) k_f



c) k_s



- ♦— Forbes
- Tinker
- ▲— Yolo Surface
- +— Yolo Vadose
- Webster
- ▽— Houghton
- Chelsea
- ×— Ohio Shale